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PROGRESS IN PHOTOGRAPHY RESULTING FROM THE WAR

By Paul W. Merrill

If the human energy and material wealth which were expended in the great war could have been devoted to the prosecution of scientific research how valuable the results would now be; how different from the actual results of devastation and want! What splendid applications of scientific knowledge to practical problems and what improvements in many technical processes would surely have been accomplished along many lines; and who knows to what extent the outlook on the great mysteries of nature might have been widened—to the future benefit of mankind!

Aside from the irreparable loss of life it is perhaps an open question whether scientific work has on the whole been injured or assisted by the war. Much research, of course, had to stop on account of the absence of investigators from their laboratories and offices. On the other hand the government, which usually regards such work as an unnecessary luxury and gives but a pittance to its prosecution, under the stress of a great emergency acknowledged its value and supplied it with funds as never before. Accordingly, certain kinds of research were vigorously pushed and were developed far more rapidly under war conditions than they would have been otherwise. The losses of the war are irretrievable and it is therefore all the more important to make the most of anything on the other side of the account. Promising novelties should be further developed and new methods of general and permanent value should be made widely available. That there is considerable material of this kind has been well known to many who were in touch with the scientific and technical aspects of the war; and this is now being made obvious by the contents of current technical periodicals. The military authorities seem to be taking a broad and wise view of the question and are allowing the publication of a great deal of material of general interest.

Photographic methods were employed in the recent war to an extent never known before in military history. This was brought about by the wonderful development of airplanes, which allowed the military photographer a choice of strategic viewpoints heretofore existing only in imagination and speculation. Before the war photography had apparently played a very minor part in the military intelligence service. In any event the United States was even less well prepared in military photography than it was in many other of the technical phases of modern warfare. The navy accomplished a little good work in aerial photography early in the war, which, however, did not become widely known. The faulty organization and mismanagement in that portion of the Signal Corps devoted to the production and operation of aircraft prevented rapid development of the art and science of military photography in the army. The inefficiency was probably due, not so much to the gross incapacity of the officers as to conditions which required the development, in a time really too short for the purpose, of an enormous organization dealing with a subject in which there was scarcely a single competent expert in the whole country. The new officers, doing the best they could under trying conditions, were hampered by the organization and methods of the war department, which are not at all adapted to the rapid development of innovations. Unfortunately also there were some officers who seemed unable to grasp the essential requirements of the situation; who gave no heed to the query "what *can* be done?" but were only concerned with "what *has* been done?" Obviously this policy was suicidal as applied to such a problem as that of aerial photography in the great war. These men retarded photographic progress considerably, but before the armistice was signed much substantial work was under way which would have been of great assistance at the front a little later.

The European nations also had been rather slow about advancing photographic technique, but actual contact with the fighting had pointed out certain egregious mistakes made early in the war and good progress was being made toward the last. However, it is not the purpose of this article to relate the photographic history of the war but to set forth some of the wartime developments in photography which seem likely to be of permanent interest to photographers, and, in particular, to those who make use of photography as an aid to scientific research.

Improvements in photographic emulsions are of vital importance to the physicist and especially to the astronomer, since many objects to be photographed are faint and available exposure times are limited. A large portion of the work is spectroscopic in character, and dry plates are required which are sensitive not only to the whole of the visible spectrum, but to a considerable range of invisible wave-lengths beyond either end. In a great many important instances scientific work is limited by the characteristics of available photographic emulsions.

It was found early in the war that aerial photographs, except those taken straight down (called verticals) from low altitudes, were adversely affected by the haziness of the air, and that satisfactory pictures from altitudes above 8000 to 10,000 feet, or long distance "obliques" at any altitude, seemed impossible even on clear days. Of course these views were just the ones of greatest value for military purposes. The cause of the difficulty and the remedy for it were readily suggested from spectroscopic principles. The haze, which makes the image of the ground indistinct, is due to sunlight scattered toward the lens by particles lying in the cone joining it to the ground. This scattered light is rich in the short wave-lengths; it is even more detrimental to the ordinary photograph than to the eye, so that the use of the longest wave-lengths possible was clearly indicated. At first orthochromatic or yellow-sensitive plates were used with good results, but before long it was apparent that for photographs from high altitudes, and especially for obliques, red-sensitive plates would be required.

This knowledge led to considerable research on color sensitive emulsions. The only practical method known at present, by which photographic emulsions can be made sensitive to the longer wave-lengths (yellow, red, and infra-red light), involves the use of certain synthetic dyes. These dyes may be mixed in the emulsion before it is coated on the plates, or they may be applied to the plates after manufacture by immersing them in solutions containing the dyes.

Commercial color-sensitive plates have long been made by mixing sensitizers in the emulsion. In an attempt to produce panchromatic plates for military purposes at least three firms succeeded in improving their previous emulsions. The most notable success of all was by the English firm of Ilford Limited. Their new pan-chromatic plate is the best of its kind which has yet been produced. Its speed to red light is especially great, and its other properties of contrast and freedom from fog make it as a whole a remarkably fine plate, that should prove very useful for many purposes including photography of the spectrum. The special technique employed in obtaining these excellent results appears to be quite new and a real step in advance of previous processes. It consists of a method of stimulating the sensitizing powers of certain dyes of the pinacyanol class. This may be done by the use of ammonia, but plates so prepared are liable to fog and will not keep. Another method, involving *auramine*, a yellow dye of the coal-tar group, as an auxiliary agent, was discovered in the Ilford laboratories by F. F. Renwick and O. Bloch; it gives increased speed and at the same time yields clean-working and reasonably stable plates. Plates prepared by this method were produced in large quantities for war photography and are now on the market under the name Ilford Special Rapid Panchromatic. This emulsion has a fairly uniform sensitivity from the ultra-violet to the extreme red. With strong exposures the action will extend as far as 7800A in the infra-red; in ordinary work it may be considered to cease at 7200A. The plate as now made is a compromise between an increase of speed and red-sensitiveness on the one hand, and ease of working and keeping properties on the other. It can be made much faster, but then becomes liable to fog and will not keep; hence it is not suited to commercial exploitation. For purposes of aerial photography in the war this plate was developed to a point where exposures thru a spectroscopically pure red filter could be obtained in one one-hundredth of a second.

The Eastman Kodak Company also produced a somewhat similar plate that was a decided improvement on the previous Wratten panchromatic emulsions. While this plate is not yet on the market, the company has offered its services in the production of special color-sensitive plates for experimental and scientific purposes, and has been very generous in responding to requests that have been sent to it. It manufactured and distributed a large number of experimental emulsions for war work.

The Cramer Dry Plate Company produced a fine red-sensitive plate of a different type. This emulsion is slower, but has more contrast, is finer grained, and works beautifully clean. Moreover, they succeeded in hardening the film in such a way that the usual hot-weather troubles of softening and frilling are practically eliminated. The emulsion may be used under conditions which are quite impossible for most emulsions; for example, development and washing at high temperatures. This property might prove of great value in the tropics, and on expeditions where the ordinary conveniences are not available. The plate, which is for sale under the name Cramer Spectrum Process, was specially prepared during the war for military use.

A laboratory method of producing color-sensitive plates is to soak ordinary plates in solutions of the sensitizing dyes. The method is not difficult, as it requires only the usual dark-room facilities. Moreover, for regions of the spectrum of greater wave-length than about 5900, plates so prepared can be made more rapid than any commercial brand (with the possible exception of the new Ilford plate at certain wave-lengths). Plates treated in this way are known as bathed or stained plates. The general characteristics of a considerable number of photographic dyes have been known for some time, largely thru the work of Eder and his associates. A number of years ago an extensive program, involving careful experimentation on the technique of bathing, was carried out by R. James Wallace[1], then connected with the Yerkes Observatory. He found that the best results were obtained by using the dye in a dilute water and alcohol solution containing a small amount of ammonia. He recommended rapid drying to produce the most sensitive plates and used a rinse in pure alcohol after the staining bath. A good deal of experimentation since that time has shown the wisdom of these details of manipulation, and no essential improvements have as yet been introduced. The use of water and alcohol is a compromise between different considerations. Other things being equal a water bath would probably produce faster plates, but the drying cannot be made rapid enough except under especially favorable conditions. Moreover the dyes flocculate very quickly in a water solution upon the introduction of ammonia, so that such a bath is inconvenient to use and with some dyes nearly impossible. An alcohol solution best holds the dye in suspension (it is a question whether or not true solution occurs), and allows the drying to take place much quicker, but alcohol so hardens the gelatine film that the dye will not enter it properly. Hence an alcohol and water bath, followed by an alcohol rinse, has been found the most favorable. War work at the Bureau of Standards showed that it was possible to use several other organic solvents instead of ethyl alcohol, but none of these was found superior to it. Since water and alcohol give slightly different spectro-sensitivity curves, quite a number of other dye solvents were tried in the hope that they might give still better sensitivities; but all such solvents, when diluted with water (in order to soften the film), seem to give practically the same curves. Excellent results were obtained with acetone and water, and fair results with methyl alcohol and a few other substances. Only those solvents which were not decomposed by the action of ammonia were tried.

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[1] *Ap. Jour.*, **26**, 299, 1907.

Presence of ammonia is found to be an essential part of the process if the greatest sensitivity is required. A number of different methods of applying the ammonia have been tried, but the Wallace process was found the most successful of all. One method, which led to interesting results in another connection, may be mentioned here. It was surmised that the dyed plates would keep better if the ammonia were omitted from the dye bath, and that the increase in speed might be obtained by a subsequent ammoniating bath. This was found to be the case, but the method was not very satisfactory; the final result was not equal to that produced by the regular Wallace method, the plates showed more defects and two separate soakings and dryings were involved instead of one. However, the increase in speed of the dyed plates upon subsequent ammoniation suggested that possibly commercial panchromatic plates could be hypersensitized by treatment with ammonia. This was tried in the spring of 1918 at the Bureau of Standards by the writer, with the assistance of Miss Barton, with excellent results. All of the plates tested had the red sensitivity enhanced, some of them to an astonishing degree. The development of this method was taken up as a war problem by Drs. Kiess and Burka of the Bureau of Standards. As the result of a large number of systematic tests the following procedure was recommended:

> Soak the plates for four minutes in a bath composed of water 75 parts, ethyl alcohol 25 parts, concentrated ammonia 3 to 4 parts. Dry rapidly in a current of air. To make certain of rapid drying the plates may be rinsed in pure ethyl alcohol for 15 seconds immediately after the ammonia bath.

The work has been further extended by Mr. Burka and is described in his doctor's thesis presented to Johns Hopkins University in 1919. The thesis will be published in the Proceedings of the Franklin Institute for January, 1920.

Unfortunately the hypersensitized plates will remain in good condition for a limited time only—a few weeks at the most. Nevertheless the original speed of the plates is so greatly increased, especially in the red, that the process should be a boon to spectroscopists and others who desire very rapid-color sensitive plates, and who are not prepared to sensitize ordinary emulsions by the use of dyes. It appears to be applicable to those emulsions in which the color sensitivity is gained by means of certain groups of the quinolinium dyes. This includes all panchromatic plates, and certain brands of orthochromatic plates.[2]

As mentioned above, certain synthetic dyes, known as sensitizing or photographic dyes, are essential to the production of emulsions capable of being affected by yellow and red light. Previous to the war practically the sole source of the most important of these dyes, with the exception of erythrosin, was the firm of Meister Lucius and Brüning, Hoechst am Main. They made a large number of dyes, including pinaverdol, pinacyanol, orthocrome T, pinachrome, pinacyanol blue, pinachrome violet, pinachrome blue, dicyanin, and dicyanin A. With the shutting off of this source of supply attempts were made to produce the more important dyes in England and in this country.

In the United States the production of photosensitizing dyes was taken up by the Chemical Section of the Science and Research Division of the Bureau of Aircraft Production, under the direction of Dr. H. D. Gibbs. The problem of the synthesis of the various dyes required for the preparation of plates used in aerial photography was assigned to Dr. Louis E. Wise of the Bureau of Chemistry, Department of Agriculture. In its solution the Bureau of Chemistry coöperated actively. The work was carried out in their laboratories by their chemists, assisted by men with chemical training assigned to them from the military service. Closely associated with Dr. Wise in the dye investigations was Dr. Elliot Q. Adams. These men deserve great credit for the excellent results which have been achieved. The first phase of the work was undertaken to find which particular quinoline derivatives were the ones to be used in making pinaverdol and pinacyanol. In a few weeks they had succeeded in producing pinaverdol, and both the iodide and chloride of pinacyanol. Important improvements were made in the German methods of preparing some of the essential intermediate compounds.

The chemical complexity of these compounds may be inferred from their formidable designations. A few samples follow: toluquinaldine methyl iodide; p-toluidine hydrochloride; alpha, gamma-di-methylquinolinium alkyl halides. The structure of pinaverdol is indicated by "1, 1', 6'-trimethyl-iso-cyanine iodide."

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[2] For further information on this method of hypersensitizing see *Circular of the U. S. Bureau of Standards*, "Color-Sensitive Photographic Plates," issued November 6, 1919.

After the signing of the armistice the work was taken over, and is now being continued by the Color Laboratory of the Bureau of Chemistry. Altogether a large number of dyes of several chemical groups have been produced. The sensitizing action of all of them has been thoroly investigated by the Spectroscopic Section of the Bureau of Standards. These tests have served to guide the chemical investigators in the synthesis of known dyes and also of new ones. Dicyanin and some other infra-red sensitizers have been produced. A new dye known as kryptocyanin sensitizes in the orange and in a narrow region from wave-length 7200 to 7700A. This latter property will prove especially useful if the dye can be used in combination with pinacyanol. It seems very probable that there exist sensitizers for the infra-red more potent than any that are yet known. The best sensitizers in other regions have a comparatively narrow region of action. If this were true for the infra-red dyes it would mean that they have not yet been discovered, for the dyes that are now being used for this region are the *red* sensitizers which have been found to give the greatest extension into the infra-red. Therefore, a thorogoing search for new agents is of much importance and would seem to have excellent chances for success.

In England the Ilford Company, with the coöperation of Sir William Jackson Pope, K.B.E., F.R.S., was very successful in duplicating the German photographic dyes and in producing new ones. During the war they produced Sensitol Green, which is identical with pinaverdol; Sensitol Red, which is pinacyanol iodide, and Sensitol Violet, a new dye having somewhat the same properties as pinacyanol. These three dyes may now be purchased from Ilford Limited. The subject of the photographic dyes has been treated in a broad way by Professor Pope, and altogether some sixty varieties have been prepared in the chemical laboratory at Cambridge. The relationship between chemical constitution and sensitizing action has been studied and a few definite regularities have appeared. The work is now being extended in the direction of preparing new sensitizers for the infra-red.

Thus the war has made England and America independent of Germany in the matter of photographic dyes. It has also stimulated research as to their constitution and properties, which is already bearing fruit in improved sensitizers for certain regions, and which is highly promising for future progress. In a few years wave-lengths of 10,000 angstroms will probably be recorded as easily as those of 7,000 are today, and it may become practicable to extend photography to 20,000 angstroms.

As in the case of sensitizing dyes, certain dyes used to produce ray filters or light screens were formerly obtained from Germany and after the outbreak of the war were no longer available. Successful efforts were made by chemists of the allied nations to produce dyes that would give the required light absorption for various uses. Mention may be made of "Eastman Yellow," a dye evolved by chemists of the Eastman Kodak Company to replace Filter K, a German dye which had been used in making the well known series of Wratten K filters. The new dye gives filters which are said to be superior in optical properties and in stability. They are being placed on the market to supplant the "K" filters in a corresponding series with the designation "EK."

In many military situations it was necessary to have the finished print in the shortest possible time after the exposed plate was received at the dark room. It was even considered important to cut down the time of development to the lowest limit. To this end quick acting developers were employed. It was, of course, also desirable to have a developer which would give the greatest possible density to underexposed plates. Certain experts believed it possible to combine the two features in a single developer. The attempt was made to accomplish this by extremely concentrated developers often containing a large amount of caustic.

There is no subject upon which there is greater lack of agreement than that of developers. Certain developing agents or methods are used by one man to give density, by another to give contrast, by another to give "detail," while others deny their virtues for these results, or may even use the same procedure for opposite effects. There is accordingly no agreement as to the value of these concentrated developers. Some of them are difficult to prepare, and are apt to give trouble with chemical and dichroic fog. The general weight of opinion, however, seems to indicate that they possess a slight but real advantage for very weak exposures; in other words, that they tend to raise the lower part of the characteristic energy-density curve above the values given by other developers, and that they may thus serve to bolster up to usefulness a negative which would otherwise be hopelessly underexposed. At the Eastman Research Laboratories and probably elsewhere these concentrated developers involving both old and new developing agents are being made the subject of extensive study, which should lead to a determination of their value for various kinds of scientific work.

War-time experience in photography from airplanes should be an aid in numerous problems in civil life. It will surely prove so in cartography and probably in many unforeseen applications in technical and scientific work. The possibility of being assured of a view of an eclipse of the Sun by being prepared to soar above intervening clouds has already attracted attention. The idea is not necessarily chimerical. In some localities the chance of securing valuable observations from an airplane would be fully as great as from a station on the ground. Nor are photographic observations out of the question. A de Haviland plane with a Liberty motor, at 10,000 feet altitude, rides more smoothly than a train, and should permit direct photographs on a small scale, especially if the plane were equipped with a gyroscopic stabilizer. Snapshots of the flash spectrum could probably be made with an apparatus such as that used by Professor Frost at Green River on June 8, 1918. A modern plane would readily surmount any ordinary fog or cumulus clouds, tho cirrus is usually too high. Aside from cirrus clouds the observer would have a wonderfully clear, dark sky. By flying in the direction in which the shadow moves the duration of totality could be increased by five or ten per cent.

Some other scientific problems involving observations from high altitudes might be open to photographic investigations from airplanes. This would be the case if the essential apparatus were light and portable and did not require a stable foundation. To reach an altitude of 15,000 to 20,000 feet, it would be easier to ascend in a suitable airplane than to go on mule back up a mountain trail, and to reach much higher altitudes it would be the only way. The polarization of light scattered by the upper air could readily be recorded by means of the polarimeter recently developed by Anderson and Babcock[3]. The ultra-violet light from the Sun and its absorption in the Earth's atmosphere might well be studied from an airplane by taking up a small spectrograph. A very interesting possibility is that of detecting the solar corona. The sky light is the only thing that prevents observation of the corona, and the sky grows rapidly darker with increasing altitude. From 25,000 feet the sky light would be considerably decreased, especially in the longer wave-lengths, and if the corona possesses any strong radiations in the region around wave-length 7000, suitable methods might make it observable. Unfortunately not much is known about the coronal spectrum in this region. The use of shorter wave-lengths would not seem very promising, in view of the skillful attempts already made by Hale from mountain peaks, but it might possibly be worth trying from higher altitudes.

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[3] *Ap. Jour.*, **50**, 228, October, 1919.

If these observations or others of the same general character should be undertaken, certain war investigations would furnish useful information. Ingenious methods of recording very accurately the vibrations encountered in airplanes were developed and applied to various types of machines. The problem of mounting cameras and other instruments to be as free as possible from the effects of vibration received considerable attention. Data on the brightness of the sky from various altitudes were gathered by Luckiesh.[4] The files of the War Department probably contain other material of value in this connection.

The reader should note that in the foregoing paragraphs no attempt has been made to describe in true proportion the photographic achievements of the war. The only aim has been to give an account of certain features which seem to be of potential value to scientific research.

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[4] *Aerial Photometry. Ap. Jour.*, **49**, 23, March, 1919.